

# PATENT ABSTRACTS OF JAPAN

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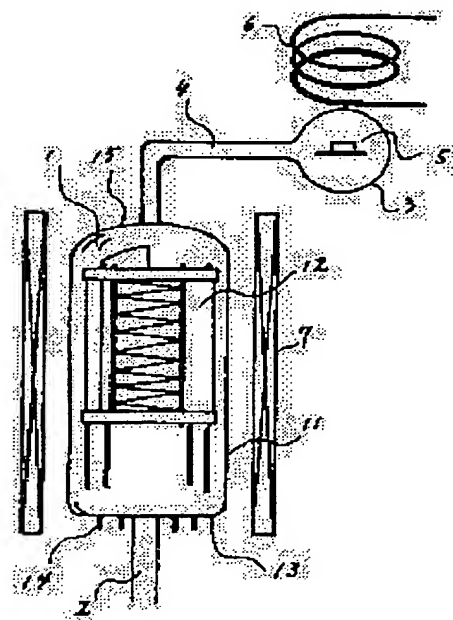
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## (54) MANUFACTURING METHOD OF PHOTOELECTRON BOOSTER TUBE

### (57)Abstract:

**PURPOSE:** To produce a photoelectron booster tube of less current leakage and noise and high photoelectric sensitivity and secondary emission rate by gradually sending alkaline metal into a photoelectron booster tube through a thin tube by heating an alkaline metal container.

**CONSTITUTION:** After evacuating the air from a booster tube 1 through an exhaust tube 2, an alkaline pellet 5 is heated with a high-frequency heater 6 to produce an alkaline metal by reduction. After keeping the booster tube 1 at a high temperature and the sealed alkaline metal container 3 at a higher temperature than that of the booster tube 1 in a furnace until the photoelectric sensitivity of the photoelectron booster tube reach a fixed level, then a thin tube 4 is cut and sealed to separate the container 3. After further keeping the photoelectron booster tube 1 at a fixed temperature for a fixed time period to discharge excessive alkaline metal, the photoelectron booster tube 1 is cooled down and the exhaust tube 2 is cut and sealed.



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⑭ 光電子増倍管の製法

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SEARCH REPORT

明 細 書

1. 発明の名称

光電子増倍管の製法

2. 特許請求の範囲

有底筒型の気密容器に、アンチモンを塗布した光陰極およびダイノード基板を組み込んだ光電子増倍管において、一方の底面に排気管を取付け、他方の底面にアルカリ源を内蔵する気密容器を細管を介して取付けると共に、上記排気管より十分排気した後、上記アルカリ源を還元し、続いて上記アルカリ源の気密容器を加熱することを特徴とする光電子増倍管の製造方法。

3. 発明の詳細な説明

従来、アンチモン-セシウムあるいはマルチアルカリ光陰極などアルカリ金属を構成物質とする光電面およびダイノードを有する光電子増倍管は、気密容器にあらかじめ蒸着などの方法で金属基板上にアンチモン層を塗布した電極と、クロム酸アルカリ、シリコン粉末と酸化アルミニウム粉末を混合し圧縮してアルカリペレットと呼ばれる

ものを組込んだ管球を十分排気した後、上記アルカリペレットを加熱してアルカリ金属を得、該アルカリ金属を前記アンチモン層に作用せしめて前記電極に光電子放出能または二次電子放出能を付与することによつて製造していた。

しかし上述したようなアルカリペレットは、急激な加熱により短時間に還元しなければ所期の量のアルカリ金属が得られないことと、長時間に亘つて所期の速度で還元する制御が極めて困難である理由により、急激にアルカリ金属を還元していた。この結果、気密容器内壁などアンチモン層以外の部分にアルカリ金属が付着し、気密容器の加熱、長時間の排気によつても完全に除去できないから不要な熱電子放出、リード線間のリーク電流を生ずる。また光電面、二次電子面の形成するとき、アンチモン層は150℃ないし200℃に加熱されているからアルカリ金属の還元と同時に発生する炭酸ガス、水、メタンその他のガスの吸着、混入により光電子放出比、二次電子放出比の優れた光電面、二次電子面が得られない。

本発明は上述のような欠点を除いた光電面の製法に関するものである。すなわち光電子増倍管の有底筒状気密容器の一方の底面に排気管を取付け、他方の底面にアルカリペレットを内蔵する気密容器を細管によつて上記光電子増倍管の容器に接続すると共に、上記排気管より十分排気した後、上記アルカリペレットを加熱して還元し、脱いて上記アルカリ源の容器を加熱してアルカリ金属を光電子増倍管の中に細管を通じて徐々に送り込むことによつてリーク電流や雑音が少なく光電感度および二次電子放出比の大きな光電子増倍管を得る光電子増倍管の製法である。

次に実施例について本発明の製法を詳細に説明する。第1図は本発明の実施例を示す図である。すなわち1は光電子増倍管で円筒状のガラス気密容器11の内部に光陰極、ダイノードおよびアノードなどの電極12が組込まれていると共に、底部13には各電極に接続されたリード線14・・・14が植設され、さらに排気管2が取付けられている。また他端の底部15にはガラス細管4

を介してガラス気密容器3が取付けられ、各ガラス気密容器1と3は連通している。5はアルカリペレットで、クロム酸セシウム、クロム酸カリウム、クロム酸ナトリウムその他アルカリ金属のクロム酸塩とシリコン、アルミナなど還元剤および緩衝剤を~~粉末~~<sup>粉状</sup>混合した後、圧縮して固型化したものを第2図に示すようなつばつきの金属容器51に投入し、円板状の金属蓋52で覆った後、適宜の間隔で点53、53・・・53において溶接して一体としたものである。

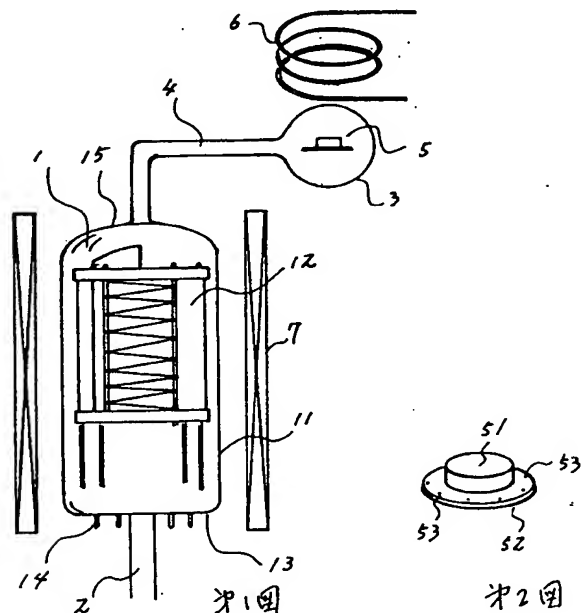
次に上記例に基き本発明の製法の工程の実施例について詳述する。排気管2を図示していない真空ポンプに接続し、必要に応じて光電子増倍管1およびアルカリペレット5の入った気密容器3を300℃以下の温度で加熱してガス出しした後、高周波誘導加熱機6によりアルカリペレット5を加熱してアルカリ金属を還元して得る。このとき光電子増倍管1は光電面形成の工程を急ぐならあらかじめ百数十度に加熱してあつてもよいが、アルカリ金属の還元と同時にアルカリペレット5に

吸収、吸着していたガスが放出するから室温状態である方が光電面への悪影響が少い。脱いて光電子増倍管1を加熱炉7で百数十度に、アルカリペレットの気密容器3を図示しない加熱炉により上記光電子増倍管の温度より高い温度に光電子増倍管が所定の光電感度に達するまで保つた後、細管4の一部において気密容器3を封じ切る。さらに所定の時間、光電子増倍管1を上記温度に保つて過剰なアルカリ金属を排気管2より排出した後、室温まで冷却して排気管2の一部において封じ切る。

以上に実施例によつて本発明を詳細に説明したが、この製法により前述した理由から、従来のような、すなわちアルカリペレットを光電子増倍管1の内部に組込んだ光電子増倍管の製法に較べてリーク電流、雑音が少なく光電変換効率の大きな光電子増倍管が得られるものである。

#### 4: 図面の簡単な説明

第1図は本発明の実施例の装置の構成図である。第2図は第1図5の拡大図である。



DOCUMENT 1:

ALKALI METAL GENERATOR

Japanese Published Examined Patent Application No. S-48-20944

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Application No. S-44-49695

Filed on: June 25, 1969

Inventor: Haruo Takashio, et al.

Applicant: Tokyo Shibaura Electric Co., Ltd.

Patent Attorney: Akira Tomioka, et al.

Brief description of the drawings

Fig. 1 is a partial cutaway perspective view describing one embodiment of the present invention. Fig. 2a and Fig. 2b are, respectively, a curve diagram showing the relationship of heating temperatures with the respective generation quantities of cesium or potassium metal vapors from the alkali metal generator of the invention. Fig. 3 is also a curve diagram showing the relationship of generating temperatures with the mixture ratio of (Ca + K)/Nb (mole ratio). Table 1 is a list comparing characteristics of various materials shown in Fig. 1.

Detailed description of the invention

The present invention relates to alkali metal generators favorably suitable for photoelectric surfaces of image pick-up tubes, photoelectric tubes and others.

Conventional alkali metal generators used in preparing photoelectric surfaces have been made by adding a single or a plurality of reducing agents to a single or a plurality of alkali metal salts to obtain a mixture through agitation, which is then appropriately pulverized. A single or a plurality of the alkali metal salts are used depending on the type of the photoelectric surface concerned, including chromate, bichromate, tungstate or molybdate combined with sodium, potassium, cesium, lithium

or rubidium. Silicon, zirconium, aluminum and boron are mainly known as reducing agents used for this purpose. In preparing the photoelectric surface, a mixture in which a reducing agent and an alkali metal salt are formulated to give a weight ratio of 2 to 1 is filled into an electrically conductive metal container at a specified quantity to give the alkali metal generator, which is placed at a specified position of a tube where a photoelectric surface is formed. Then, at an appropriate time in the course of preparing the photoelectric surface, the metal container is heated through electrical conduction or high frequency induction heating, thereby isolating alkali metals. The thus-prepared alkali metal is able to move easily to a previously arranged photoelectric matrix surface, for example, an antimony film surface, by keeping at least a part of the outer periphery of the tube at an appropriate temperature, thus resulting in formation of the photoelectric surface through predetermined processes.

The metal container takes such a shape as shown in Fig. 1, the container 1 is fabricated by making a thin conductive plate 2 into a spiral shape to form a hollow body for accommodating a mixture 3, then giving a spot welding to a polymerization end 4 in the longitudinal direction of the hollow body and flatly crushing an opening of the body.

A space between the welded spots is used for releasing isolated alkali metals generated by the chemical reaction. It is necessary to operate the alkali metal generator at temperatures close to those causing an exothermic reaction and a large amount of alkali vapor generation or either of them in order to obtain a substantial quantity of the alkali metal.

In the alkali metal generator, the alkali metal must be deposited at an appropriate quantity on a photoelectric surface in order to improve characteristics of the surface, for example, the photoelectric sensitivity. Thus, an abrupt generation of an alkali metal makes it difficult to adjust a quantity of alkali which is to deposit on the photoelectric surface. For the purpose of alleviating exothermic phenomena, tungsten is added

as a buffering agent, in addition to the silicon, aluminum or zirconium. Further, an abrupt generation of an alkali metal not only makes it difficult to adjust the quantity of the alkali metal but also releases gas in the great quantity. The release of gas will deteriorate photoelectric characteristics, for example, photoelectric sensitivity. Therefore, for the purpose of preventing such release of gas, zirconium and others having getter effects are often used as a reducing agent.

Since alkali deposition on a target, secondary electron intensifier electrode and others may affect the shelf life of a tube and the image quality during the process of generating alkalis such as cesium, irrespective of the alkali quantity, an ease in controlling the reaction is a critical factor in manufacturing image orthicon, a type of image pick-up tube.

Although depending on the type of the tube concerned, characteristics necessary for an alkali metal generator include, in general, (1) a greater photoelectric sensitivity, (2) a stable generation state, (3) lower generation temperature, (4) freedom from puncture or fusion, (5) relatively no changes in the generation state under preliminary heating conditions, (6) a small quantity of gas release up to the stage of generation, (7) ease in controlling a state of generation (no abrupt generation), (8) workability if the reducing agent has getter effects, (9) a relatively small volume necessary for generating a specified quantity of alkali, (10) substantially no need for a buffering agent, (11) no possibility of explosion like zirconium, (12) lower vapor pressure degree of reactants such as those other than alkali metals, and (13) a greater yield of alkali metals generated.

The above characteristics were not satisfied where conventional reducing agents such as silicon, zirconium, titanium and aluminum were used as the alkali metal generator.

More particularly, an alkali metal generator in which silicon Si is used as a reducing agent is high in generation temperature, which is 900°C as shown in Table 1, quite unstable in a generation state and accompanied by a very abrupt

exothermic reaction. The alkali metal generator may sometimes cause puncture or fusion of a nickel container used for filling a mixture. A higher temperature for effecting the gas generation may damage some parts inside the tube, for example, a target and others, which are not favorable. Additional gas generation without a preliminary heating could result in a more intense reaction and almost always entail puncture or fusion. Although, a preliminary heating is carried out, the reaction greatly changes every  $\pm 10^{\circ}\text{C}$  in response to a slight change in the preliminary heating conditions. Further, cesium or potassium may be generated at a greatly different quantity and accompanied by possible risk of puncture or fusion. It is, thus, extremely difficult to control the state of alkali metal generation. A lower bulk density of silicon requires a larger volume container for generating a specified quantity of metal, thus making it difficult to miniaturize the tube, and may result in a gas generation source or a great quantity of gas generation or gas release. Further, this alkali metal generator has many other disadvantages such as a lower yield of alkali metals and a lower photoelectric sensitivity which may be due to a great quantity of gas release as mentioned above.

Further, in an alkali metal generator in which zirconium is used as a reducing agent, the generation temperature is  $900^{\circ}\text{C}$  or higher as shown in Table 1, and the generation state is subject to changes depending on preliminary heating conditions, thus rendering it relatively difficult to control the generation state. A relatively lower bulk density of zirconium requires a large-sized container and has a certain quantity of gas release. Therefore, the alkali metal generator is not excellent in yielding alkali metals and is relatively lower in sensitivity. Further, zirconium is disadvantageous in that it may explode, when rubbed, and mixture through agitation with an alkali metal compound is extremely difficult. Where zirconium is mixed not mechanically but as a dry system through agitation, relatively coarse powders of zirconium should be agitated and mixed slowly on paper or others for prevention of

the possibility of explosion. However, an insufficient agitation and mixture of zirconium with an alkali metal compound will result in poor uniformity.

In some alkali metal generators, a state of alkali generation may also result in a poor uniformity. Zirconium is also disadvantageous in that use of the coarse powders makes smaller the surface of zirconium involved in the reaction, thus necessitating a relatively large quantity of the mixture with an alkali metal for generating a specified quantity of the alkali metal. Zirconium mixed as a wet system would be helpful in preventing the possibility of explosion but in reality cannot be used because an alkali metal compound will be dissolved with water. In addition, where alcohol is used, a minute moisture content contained in the alcohol may change an alkali metal compound and aggregation occurring upon drying may affect uniformity of the alkali metal, thus resulting in another disadvantage, or a poor uniformity of the potassium generation state.

The present invention is to provide an alkali metal generator wherein niobium is used as a reducing agent to remove the disadvantages.

More particularly, the alkali metal generator is made by filling into an electrically conductive metal container having several minute pores a mixture in which niobium powder is added to an alkali metal salt powder, for examples, a mixture made up of cesium chromate and potassium chromate so as to give a mole ratio of  $(Cs + K)/Nb = 0.01$  to 5

A detailed explanation will be hereinafter made for the invention by referring to the embodiments. A mixture with  $Cs/K = 4S$   $(Cs + K)/Nb = 0.1$  of mole ratio is prepared on the basis of a mixture of  $(Nb + Cs_2CrO_4 + K_2CrO_4)$  in which niobium is used as a reducing agent. Then, another mixture is prepared with the similar mole ratio as the mixture with niobium wherein silicon and zirconium are used as a reducing agent to make a comparative evaluation. Fig. 2a and Fig. 2b show cesium and potassium generation states at individual temperatures in these



three mixtures. As shown in the figure, the curves showing cesium and potassium generations are steep at the rising point in the case of cesium or silicon, narrow in the temperature range, showing a possibility that gas may be generated in a great quantity and at one time. These curves in the case of zirconium show that the gas generation is absolutely lower at about 900 to 1,000°C. In contrast, in the case of niobium, the reaction can be easily controlled because the gas generation is found at a wide temperature range and is stable.

More particularly, in an alkali metal mixture prepared by adding niobium as a reducing agent, the alkali metal is generated at 780°C, which is lower than the temperature at which silicon or zirconium is generated, as shown in the Table 1. Thus, the alkali metal generator is much less frequently damaged due to heating for parts inside the tube than a generator in which other substances are used as a reducing agent. The alkali metal generator is stable in gas generation, which can be easily controlled, and completely free of fusion or puncture of the container. The gas generation does not undergo any change at all even when preliminary heating conditions vary. Further, no fusion or puncture is found in the container even when no preliminary heating is carried out, without any substantial change found in the gas generation. A greater bulk density of niobium needs a smaller volume for obtaining a specified quantity of a mixture and therefore a smaller-sized container, contributing to a miniaturization of the tube. Further, gas is released at a very limited quantity up to the stage of gas generation, the alkali metal is yielded at rate of 80% or higher, and the photoelectric sensitivity is increased.

Unlike zirconium, niobium is free of the possibility of explosion and stable in the generation, which can be easily controlled. Therefore, niobium does not need a buffering agent which is required in tungsten.

However, it should be added that it is possible to inhibit generation although to a slight extent, when tungsten W or aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is added in a weight ratio of about 10%.

Thus, a buffering agent may be added in compliance with temperatures and generation characteristics required.

Further, niobium as a reducing agent is mixed with a mixture of cesium chromate with potassium chromate at a variety of ratios (mole ratio) to give a mixture, which is used to determine generation temperatures. The results are shown in Fig. 3. As shown in the figure, it has been experimentally demonstrated that better results are obtained at a mixture ratio of  $(Cs + K)/Nb = 0.01$  to 5. An experimental evaluation is also made for a mole ratio of  $Cs/K$ , finding that better photoelectric sensitivity is obtained at  $Cs/K = 0.1$  to 20.

In addition to the previously-described chromate, alkali metal salts such as bichromate, tungstate and molybdate may be used as metal salts of cesium and potassium, the effect of which is similar to that obtained when chromate is used, as described before.

What is Claimed is;

An alkali metal generator wherein cesium metal salt, potassium metal salt and niobium are mixed so as to give a mole ratio of  $(CS + K) / Nb = 0.01$  to 5 and filled into an electrically conductive metal container.

Table 1

Mixture	Nb +CS <sub>2</sub> CrO <sub>4</sub> +K <sub>2</sub> CrO <sub>4</sub>	Si +CS <sub>2</sub> CrO <sub>4</sub> +K <sub>2</sub> CrO <sub>4</sub>	Zr +CS <sub>2</sub> CrO <sub>4</sub> +K <sub>2</sub> CrO <sub>4</sub>
Composition ratio (mole ratio)	CS/K = 4 (CS+K)/Nb = 0.1	CS/K = 4 (CS+K)/Si = 0.1	CS/K = 4 (CS+K)/Zr = 0.1
Photoelectric sensitivity NA/Lm	100n = 5	70n = 5	80n = 5
Generation state	Extremely stable	Unstable	Stable
Generation temperature °C	Approx. 780	Approx. 900	Approx. 900
Puncture, fusion	Not found at all	Sometime found	Not found
Generation state depending on preliminary heating conditions	Substantially unchanged despite change in preliminary heating conditions	Changes greatly	Changed
Gas release up to a stage of gas generation	Very small	Great	Medium
Control of generation state	Easy	Difficult	Normal
Getteraction of reducing agent	Great	Small	Great
Bulk density	2.4	0.9	1.8
Necessity for buffering agent	Not found	Found	Preferably required
Explosion risk	Not found	Not found	Found
Yield of alkali metal	Great	Small	Medium